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COPOLYMERIZATION OF PEROXY DERIVATIVES OF DIOXYDIPHENYLPROPANE DIGLYCIDYL ETHER MONOMETHACRYLATE WITH STYRENE

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Abstract. The copolymerization reaction of peroxy derivatives of dioxydiphenylpropane diglycidyl ether monomethacrylate with styrene has been studied at 333 K in the medium of toluene using azo-bis-isobutyric acid dinitrile as an initiator at different molar ratio of the initial monomers. The reaction rates have been determined and copolymerization constants have been calculated. The structure of the synthesized copolymers was confirmed by chemical and IR-spectroscopic analyses.

Keywords: peroxide, monomethacrylic derivative of dioxydiphenylpropane diglycidyl ether, styrene, copolymerization, IR-spectroscopy.

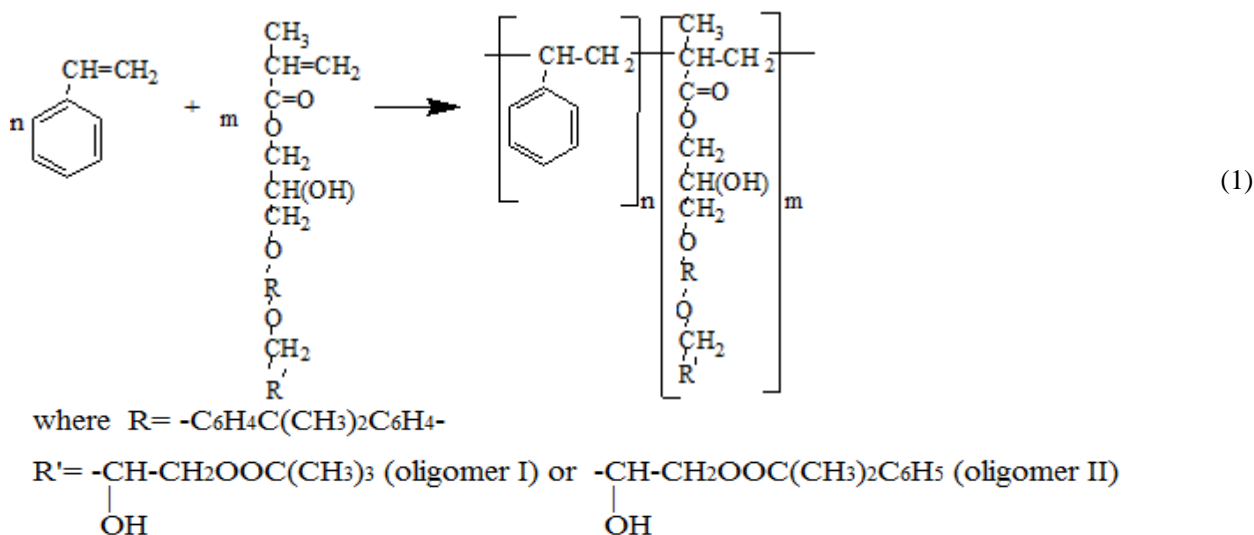
1. Introduction

The presence of methacrylic acid fragments in the molecules allows to consider them as monomers [1-3]. If

one of the monomers contains the reactive functional group, apart from the bond capable of polymerization, then such copolymer may be the initial material for comb-polymers production [4]. Oligomer with unsaturated methacrylic bond and peroxy group [5] may be used as the mentioned monomer. The presence of methacrylic groups in the oligomer structure allows to use it as a comonomer in polymerization reaction preserving a peroxy group. Actually the polymerization of methacrylic oligomer should proceed in the presence of other monomer, styrene for example.

This work deals with copolymerization of peroxy derivatives of dioxydiphenylpropane diglycidyl ether monomethacrylate with styrene according to Eq. (1).

Copolymerization in the solution was studied using toluene as a reactive medium. Azo-bis-isobutyric acid dinitrile (AAD) was used as a copolymerization initiator.



2. Experimental

2.1. Materials

Oligomer **I** and oligomer **II** were synthesized in accordance with the procedure described in [5]. For the synthesis of oligomer **I** we used 100 g of dioxydiphenylpropane diglycidyl ether monomethacrylate and 71.09 g of *tert*-butyl hydroperoxide dissolved in 350 ml of 2-propanol. The used catalyst system consists of 3.23 g of 18-Crown-6 as 25% aqueous solution and 3.39 g of ZnCl₂ as 20% aqueous solution. For oligomer **I**: molecular weight (M_n) is 510 g/mol (cryoscopy, dioxane); active oxygen content [O]_{act} is 2.3 %; bromine number (*b.n.*) is 27.5 g Br₂/100 g product.

Oligomer **II** was synthesized in the same way using 100 g of dioxydiphenylpropane diglycidyl ether monomethacrylate, 123 g of isopropylbenzene hydroperoxide, 3.4 g of 18-Crown-6, 3.5 g of ZnCl₂ and 250 ml of 2-propanol. The characteristics of the synthesized oligomer **II** are: M_n 593 g/mol (cryoscopy, dioxane); [O]_{act} 3.0 %; *b.n.* 29.3 g Br₂/100 g product.

Styrene was purified by alkali followed by distillation at 322–323 K and residual pressure of 3–4 GPa. For styrene: $n_D^{20} = 1.5463$; $d_4^{20} = 0.9062$.

ZnCl₂ and AAD were used as received without additional purification. 18-Crown-6 and toluene were of P.A. grade.

2.2. Copolymerization and Analysis Methods

The copolymers were synthesized *via* radical copolymerization of styrene and oligomer **I** or **II** in toluene medium at 333 K. The AAD concentration was $5.6 \cdot 10^{-2}$ mol/l (2.95 % relative to monomers mixture). The copolymerization kinetics was studied in completely soldered calibrated dilatometers with the volume of 15–50 ml and scale factor of 0.05 ml. Before and after loading the dilatometers were cooled, vacuumed, filled with argon and soldered. The process temperature was held by means of water thermostat with the accuracy of ± 0.1 K. The process was controlled by dilatometer indications. To check data accuracy the additional gravimetric investigations of monomers conversion were carried out after dilatometer cooling and reaction mass unloading. Copolymers were three times precipitated in hexane, dried at room temperature and then under vacuum till the weight became constant [6].

Monomers conversion is determined using Eq. (2):

$$S = \frac{\Delta V}{V \cdot k} 100 \% \quad (2)$$

where V – initial volume of monomers at the definite temperature, ml; ΔV – change in volume at the definite time, ml; k – average contract ratio for investigated monomers at the definite temperature [7].

Polymerization rate W_p (%/s) was determined according to the slope angle of the tangent to the curve represented the dependence of conversion on time in the steady area [6]. The error was 5–7 %.

Monomers conversion was additionally controlled by a gravimetric method and calculated according to Eq. (3):

$$S = \frac{M_p}{M_m} 100 \% \quad (3)$$

where M_p – polymer weight determined by gravimetry, g; M_m – monomers weight in the initial mixture recalculated for sample weight, g.

Active oxygen content in the synthesized copolymer was determined according to the procedure described in [8].

Fineman-Ross method was used to calculate copolymerization constants [6]. According to the mentioned method the copolymer composition may be calculated as follows:

$$\frac{m_1[M_1]}{m_2[M_2]} = \frac{[M_2] + r_1[M_1]}{[M_1] + r_2[M_2]} \quad (4)$$

Designating $m_1/m_2 = f$, and $[M_1]/[M_2] = F$, Eq. (4) may be represented as follows:

$$F(1-f) = r_2 - F^2 \cdot f \cdot r_1 \quad (5)$$

Plotting $-F(1-f)$ vs. $F^2 f$ we find the copolymerization constants: slope angle is equal to r_1 and segment which is cut off at ordinate axis corresponds to r_2 with an opposite sign.

2.3. IR-Spectroscopy

IR-spectroscopic investigations were carried out using Specord M-80 spectrophotometer. (Zeiss, Germany). The samples were prepared as the films formed from the copolymers solution in acetone. The films were applied over KBr plates (layer thickness was 0.03 mm). Spectra were recorded in the area of 4000–600 cm⁻¹, integration time was 1 s.

3. Results and Discussion

3.1. Oligomers I and II Copolymerization with Styrene

Copolymerization of oligomers **I** and **II** with styrene was studied according to the procedure described in Subsection 2.2. The copolymerization conditions are given in Table 1.

The experimental results obtained according to above-mentioned procedure are represented in Figs. 1 and 2. So, copolymerization process consists of two stages. The curve corresponding to the second stage is sharper. It means that partial decomposition of peroxy groups in oligomers **I** and **II** is possible during copolymerization. At the second stage these groups accelerate the polymerization of styrene and oligomers as well. The reaction rates determined from Figs. 1-2 are represented in Table 2.

If we compare data from Table 2, we observe the identity of copolymerization rates for oligomers **I** and **II**. At the same time values of W_2 rates are plotted on the straight line and values of W_1 do not submit straight dependence (Figs. 3 and 4).

If we analyze Eq. (1) we see that the synthesized copolymers must have free peroxy groups in the side branches. To confirm this fact we analyze the active oxy-

gen content in the synthesized products according to the procedure described in [8]. The obtained results are represented in Table 3.

The results from Table 3 show that at the content of 5 mol % of oligomer **I** in the initial mixture the active oxygen content is 5.5 %. The further increase in oligomer concentration does not considerably increase the amount of peroxy groups in the copolymer indicating the uniform distribution of initial monomers fragments in the synthesized copolymer.

3.2. IR-Spectroscopic Investigations of the Copolymers Structure

IR-spectroscopy was used to determine the copolymers structure. The used procedure is described in Subsection 2.3 and some spectra are given in Figs. 5 and 6.

Table 1

Composition of the reaction mixture and copolymerization conditions

Sample number	Monomers content in the initial mixture, mol %	
	Oligomers I or II	Styrene
1	5	95
2	10	90
3	30	70
4	50	50
5	70	30
6	90	10

Notes: AAD concentration is 2.95 wt % relative to monomers content; copolymerization temperature is 333 K; time is 470 min; reaction medium – toluene; total concentration of monomers in the solution is 0.07 mol/l.

Table 2

Rates of oligomers **I and **II** copolymerization with styrene**

Sample number	Oligomers content in the initial mixture, mol %	Oligomer I		Oligomer II	
		W_1	W_2	W_1	W_2
1	5	0.1639	0.0219	0.1096	0.0609
2	10	0.1203	0.0200	0.1129	0.0307
3	30	0.5115	0.0415	0.5137	0.0405
4	50	0.5034	0.0496	0.5154	0.0451
5	70	0.7740	0.0425	0.7751	0.0449
6	90	0.0969	0.0693	0.0342	0.0178

Table 3

Active oxygen content for oligomer **I–styrene copolymers**

Sample number	Oligomer I amount, mol %	$[O]_{act}$, %
1	5	5.5
2	10	5.7
3	30	5.8
4	50	6.0
5	70	6.1
6	90	6.3

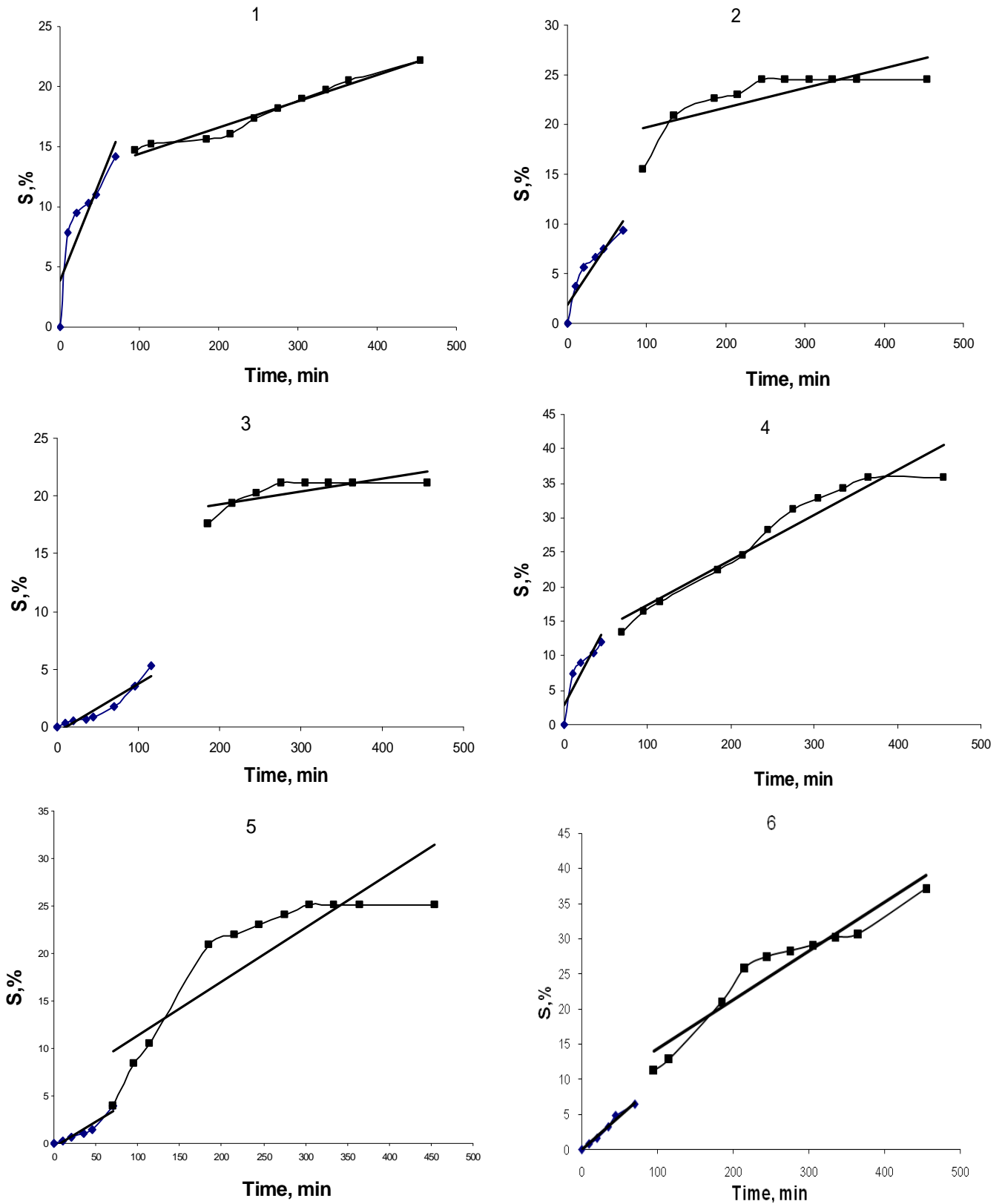


Fig. 1. Dependence of monomers conversion on copolymerization time and oligomer I content (mol %): 5 (1); 10 (2); 30 (3); 50 (4); 70 (5) and 90 (6)

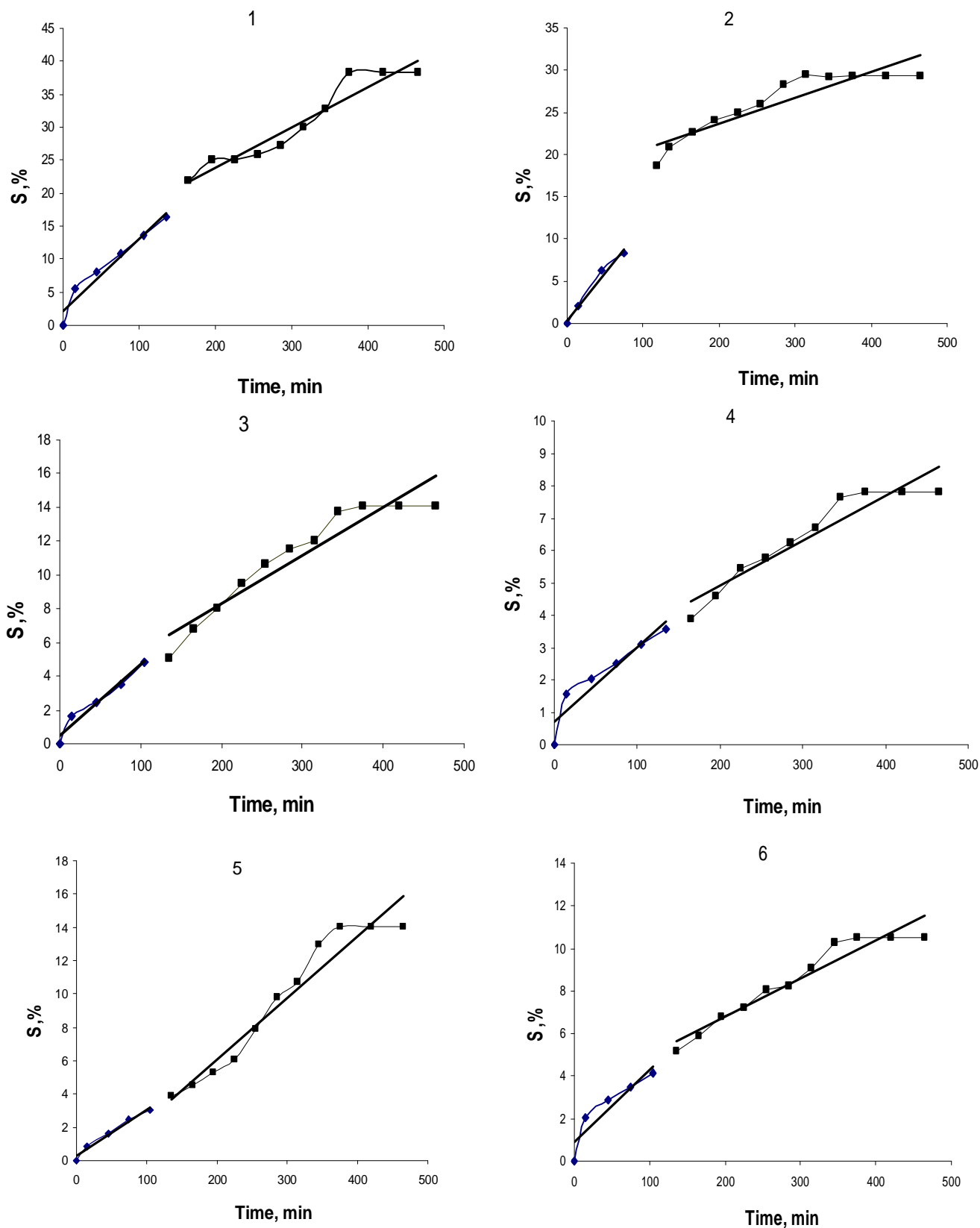


Fig. 2. Dependence of monomers conversion on copolymerization time and oligomer II content (mol %): 5 (1); 10 (2); 30 (3); 50 (4); 70 (5) and 90 (6)

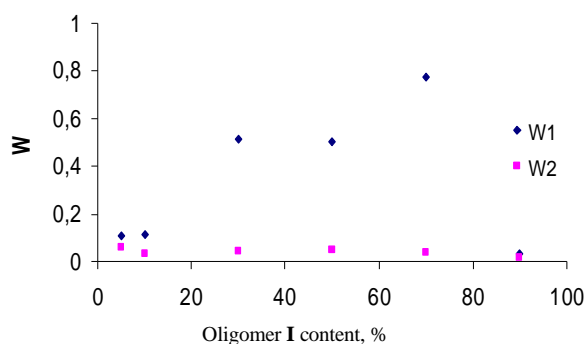


Fig. 3. Copolymerization rate vs. oligomer I content

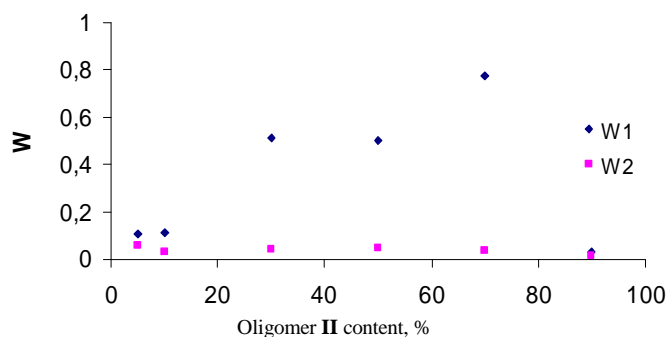


Fig. 4. Copolymerization rate vs. oligomer II content

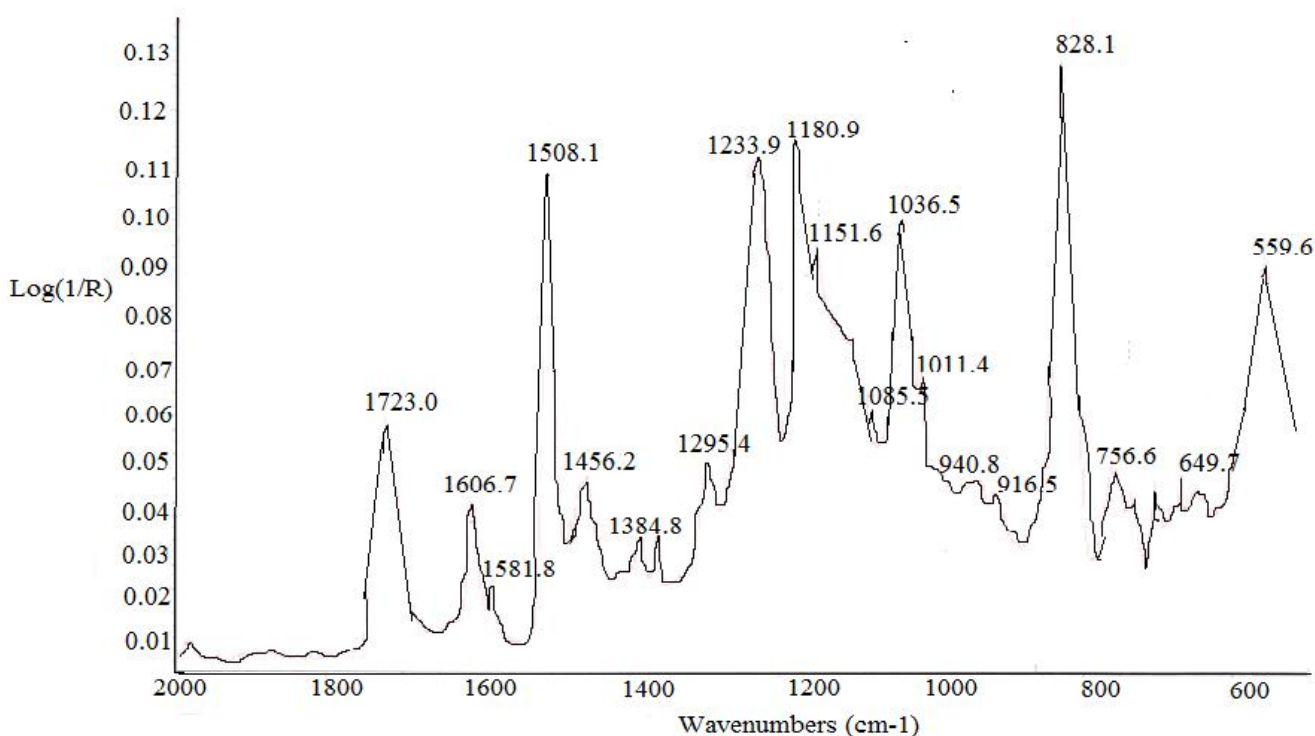


Fig. 5. IR-spectrum of the copolymer obtained according to the experiment No.6 (Table 1) within the range of 2000–600 cm^{-1}

In the spectrum of the copolymer oligomer I–styrene (Table 1, sample No.6) within the range of 2000–600 and 4000–2200 cm^{-1} (Figs. 5 and 6) the weak absorption band at 8560 cm^{-1} is observed indicating the presence of peroxy groups. The hydroxy group is confirmed by the absorption band at 3449 cm^{-1} ; the ester group – at 1723 and 1234 cm^{-1} indicating the presence of carbonyl and C–O–C groups, respectively. Benzene rings in the fragment of oligomer I are confirmed by absorption band at 1606 cm^{-1} . The introduction of styrene molecules is confirmed by the bands at 1456 and 1581 cm^{-1} corresponding to the stretching vibrations of benzene ring in a styrene fragment.

Thus, on the basis of IR-spectroscopic investigations we may assert that copolymers with fragments of styrene and dioxydiphenylpropane diglycidyl ether are obtained *via* copolymerization of peroxy derivatives of dioxydiphenylpropane diglycidyl ether monomethacrylate with styrene. Such copolymers are reactive ones due to the presence of labile peroxy groups in the side chains. The presence of peroxy groups allows to use them for the production of grafted polymers and cross-linking agents of various polymeric systems with styrene and dioxydiphenylpropane diglycidyl ether fragments in their structures.

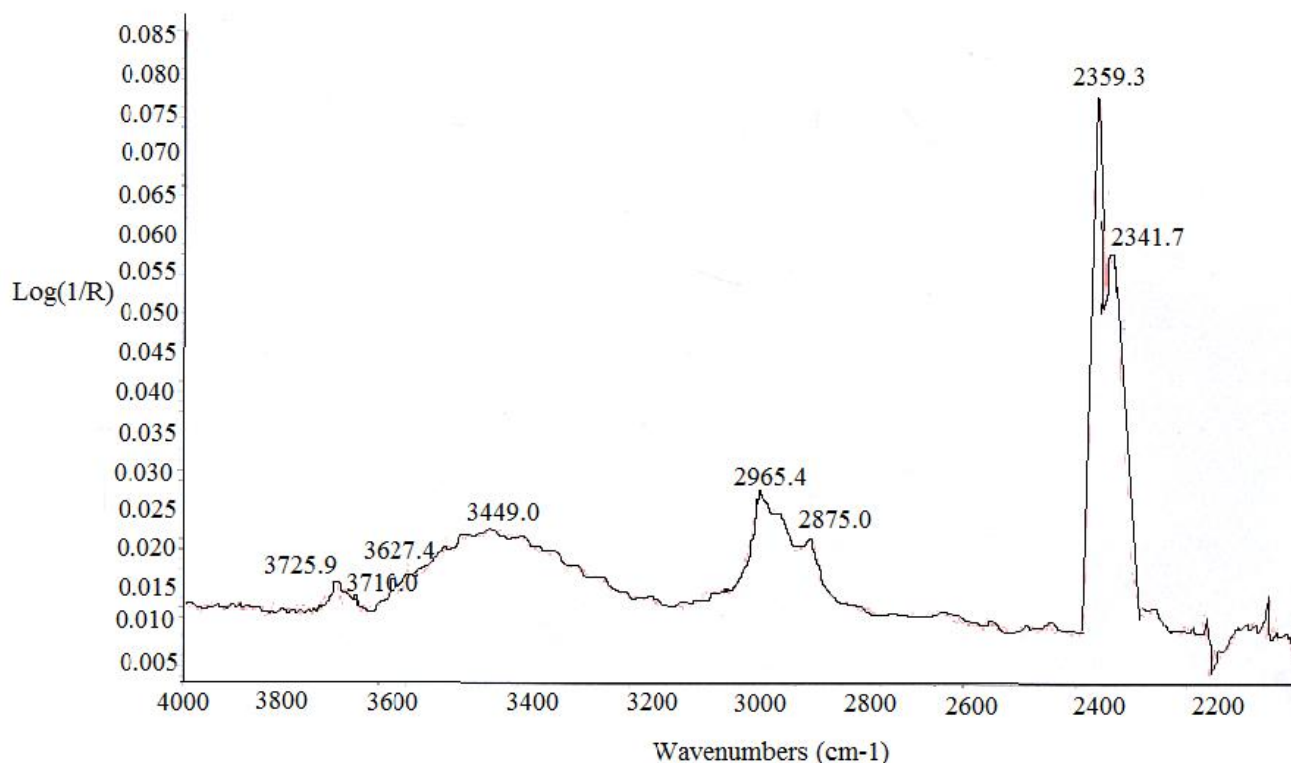


Fig. 6. IR-spectrum of the copolymer obtained according to the experiment No.6 (Table 1) within the range of 4000–2200 cm^{-1}

4. Conclusions

We synthesized new copolymers with peroxy groups in the side chains *via* copolymerization of peroxy derivatives of dioxydiphenylpropane diglycidyl ether monomethacrylate with styrene. The copolymerization process of the mentioned monomers consists of two stages. Copolymerization rates of both stages were calculated. The dependence of copolymerization rates on the content of peroxy derivatives of dioxydiphenylpropane diglycidyl ether monomethacrylate was determined. The active oxygen content is within 5.5–6.3 % and depends on peroxy monomer amount. The structure of the synthesized copolymers is confirmed by IR-spectroscopy. The presence of peroxy groups is confirmed by the absorption band at 869 cm^{-1} ; hydroxy groups – at 3449 cm^{-1} ; ester groups – at 1723 and 1234 cm^{-1} . The presence of styrene fragment is confirmed by the absorption band at 1456 and 1581 cm^{-1} corresponding to the stretching vibrations of benzene ring in the styrene fragment.

References

- [1] Havelka K. and McCormick C. (Eds.): Specialty Monomers and Polymers: Synthesis, Properties, and Applications. American Chemical Society, NY 2000.
- [2] Simon H.: Pat. USA 4983689, Publ. Jan. 08, 1991.
- [3] Iatsyshyn O., Astakhova O., Shyshchak O. *et al.*: Chem.&Chem. Techn., 2013, **7**, 73.
- [4] Percee V., Rinaldi P. and Auman B.: Polym. Bull., 1983, **10**, 215.
- [5] Bratychak M., Iatsyshyn O. and Kochubei V.: Ukr. Khim. Zh., 2012, **78**, 20.
- [6] Toroptseva A., Belgorodskaya K. and Bondarenko V.: Laboratornyi Praktikum po Khimii Vysokomolekulyarnykh Soedineniy. Khimia, Leningrad 1972.
- [7] Gladyshev G. and Popov V.: Radikalnaya Polimerizacia pri Glubokiykh Stepenyah Prevrashchenia. Nauka, Moskva 1974.
- [8] Antonovsky L. and Buzlanova M.: Analiticheskaya Khimia Organicheskyykh Peroksidnykh Soedineniy. Khimia, Moskva 1978.

**КОПОЛІМЕРИЗАЦІЯ ПЕРОКСИДНИХ
ПОХІДНИХ МОНОМЕТАКРИЛАТУ
ДИГЛІЦИДІЛОВОГО ЕТЕРУ
ДИОКСИДИФЕНІЛПРОПАНОУ ІЗ СТИРОЛОМ**

***Анотація.** Вивчена реакція кополімеризації пероксидних похідних монометакрилату дигліциділового етеру диоксидифенілпропану із стиролом за температури 333 К у середовищі толуолу з використанням як ініціатор динітрилу азо-біс-ізомасляної кислоти та*

різного мольного співвідношення вихідних мономерів. Встановлені швидкості реакції та розраховані константи кополімеризації. Структура синтезованих кополімерів підтверджена хімічними та ІЧ-спектроскопічними методами дослідження.

***Ключові слова:** пероксид, монометакрилатна похідна дигліциділового етеру диоксидифенілпропану, стирол, кополімеризація, ІЧ-спектроскопія.*